

PATENT ABSTRACTS OF JAPAN

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(54) DYE SENSITIZED SOLAR BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a regeneration dye sensitized solar battery which can be practically used wherein porphyrin derivatives and their metal complexes are used and which has high photovoltaic conversion characteristics.

SOLUTION: In the solar battery in which an electrolyte is filled between a pair of electrodes wherein a transparent electroconductive film having a porous semiconductor film in an inner side surface is assumed as one side of electrodes and a metal film is assumed as the other side of electrodes and wherein a current circuit is formed between both electrodes by irradiate from the transparent electroconductive film side at least one kind of pigment selected from porphyrin compounds expressed in a formula (R is hydrogen atom or acid substituted group) and their metal complexes is carried in fine pores of porous semiconductor film.

CLAIMS

[Claim(s)]

[Claim 1] In a solar cell which uses as one electrode a transparent conducting film which has porosity semiconductor membrane in an inner surface inserts an electrolyte between electrode pairs which use a metal membrane as an electrode of another side irradiates with light from the transparent conducting film side and makes a current circuit form among two poles it is a general formula in fine pores of porosity semiconductor membrane. [Formula 1]

The dye-sensitized solar cell making at least one sort of coloring matter chosen from the porphyrin compounds expressed with (R in a formula is a hydrogen atom or acidic substituent) and those metal complexes support.

[Claim 2] The dye-sensitized solar cell according to claim 1 whose R in a general formula is a carboxyl group.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention has high photoelectric conversion efficiency and relates to the dye-sensitized solar cell which can supply photoelectric current stable moreover.

[0002]

[Description of the Prior Art] The type which a solar cell is a photoelectric cell with which the purpose of exploiting the energy of sunlight is presented and is used former most widely Pn junction is made to form near the surface with the large light-receiving surface of a semiconducting crystal or an amorphous board and the external circuit which irradiates with visible light and connects p field and n field is made to generate current toward n from p. As a semiconducting crystal in this case although many silicon is used the manufacturing process of silicon is an energy many consumption type intrinsically and since harmful silane gas is used a problem is also in respect of environmental protection and also there is a fault that a manufacturing cost is high.

[0003] By the way in 1991 gray TSUERU and others of Switzerland (Graezel) The electrode which made the surface of the porosity titanium dioxide thin film with large surface area absorb ruthenium bipyridine carboxylic acid coloring matter is used Since the dye-sensitized solar

cell was announced and there have been the strong points such as that there is no fear of environmental pollution that a manufacturing cost is cheap and having high photoelectric conversion efficiency a reproduced type dye sensitizing photoelectric conversion cell has come to attract attention. However although what the chlorophyll derivative the zinc complex of porphyrin etc. made the optical-pumping center until now is proposed as this dye-sensitized solar cell these may be satisfied in order to present practical use as a solar cell since the photoelectric transfer characteristic is low.

[0004]

[Problem(s) to be Solved by the Invention] This invention is a basis of such a situation and is made for the purpose of providing the utilizable reproduced type dye-sensitized solar cell using the porphyrin derivatives which have a high photoelectric transfer characteristic and those metal complexes.

[0005]

[Means for Solving the Problem] A result of this invention persons having manufactured a metal complex of various porphyrin derivatives and having examined many things about the photosensitization operation New 510 and 1520 **TETORA phenylporphyrin or its derivative Or when that metal complex is used as coloring matter of a dye-sensitized solar cell it finds out that a solar cell which shows a high photoelectric transfer characteristic and can supply stable photoelectric current is obtained and came to make this invention based on this knowledge.

[0006] That is this invention is a general formula in fine pores of porosity semiconductor membrane in a solar cell which uses as one electrode a transparent conducting film which has porosity semiconductor membrane in an inner surface inserts an electrolyte between electrode pairs which use a metal membrane as an electrode of another side irradiates with light from the transparent conducting film side and makes a current circuit form among two poles. [Formula 2]

The dye-sensitized solar cell making at least one sort of coloring matter chosen from the porphyrin compounds expressed with (R in a formula is a hydrogen atom or acidic substituent) and those metal complexes support is provided.

[0007]

[Embodiment of the Invention] Next an embodiment of the invention is described according to an accompanying drawing. Drawing 1 is one example of the structure of this invention solar cell a sectional view for being

shown and between two glass substrates (the transparent substrate 1 and 7 for example glass substrates) The transparent conducting film 2 the porosity semiconductor membrane 3 the electrolyte 5 and the metal membrane 6 are arranged one by one and said semiconductor membrane 3 is formed in porosity and adsorption support of the porphyrin compound expressed with said general formula (I) in the fine pores or its metal complex is carried out. 8 is a current circuit and 9 is an ammeter.

[0008] As a material of the above-mentioned transparent electric conductor 2 the complex of the tin oxide and it and indium oxide is used for example. As a material of the semiconductor membrane 3 titanium oxide, a zinc oxide, tantalum oxide etc. are used. This semiconductor membrane 3 needs to form as porosity. The semiconductor membrane which has such porosity semiconductor membrane on the surface For example journal physical chemistry (J. Phys. Chem.) the 94th volume and the method indicated to 8720 pages (1990) are referred to Melt titanium tetraisopropoxide in the mixture of 2-propanol, deionized water and nitric acid, hydrolyze and a stable titanium oxide colloidal solution (particle diameter of about 8 nm) is prepared After mixing this solution with TiO_2 impalpable powder (the product made by Japanese Aerosil trade name "P-25") and a polyethylene glycol and carrying out spin coating of this mixture on semiconductor membrane it can manufacture by calcinating above 500 °C.

[0009] Next as a material of the metal membrane 6 used as a counter electrode although aluminum, tin, silver, copper etc. are used especially a desirable thing is platinum. This metal membrane 6 can form metal chemical vacuum deposition or by carrying out a physical vapor deposition for example on a glass substrate and other transparent substrates.

[0010] In this invention it is required to make at least one sort of coloring matter chosen from the porphyrin compound expressed with said general formula (I) in the fine pores of the aforementioned porosity semiconductor membrane 3 and its metal complex support. As a metal complex of this porphyrin compound it is a general formula for example. [Formula 3]

The metal complex expressed with (a hydrogen atom or acidic substituent at least one sort of ligands as which X is chosen from an alkoxy group, an aryloxy group, an acyloxy group and a halogen atom and M of R in a formula are Mo, Cr, Nb or W) can be mentioned. General formula HX' (III) after making the carbonyl compound of Mo, Cr, Nb or W react to the porphyrin

compound which the metal complex expressed with this general formula (II) is a new molecular entity of literature non-******for example is expressed with said general formula (I) or its derivative

It can manufacture by processing with a compound expressed with (X' in a formula is an alkoxy group an aryloxy group an acyloxy group or a halogen atom) and processing by hydrogen halide further according to a request.

[0011] Although R in a porphyrin compound which is this general formula (I) or (II) and is expressed or its metal complex is a hydrogen atom or acidic substituent as this acidic substituent there are a carboxyl group sulfonic acid residues sulfonate residues sulfuric acid residues sulfate residue etc. for example. M is a metal atom which can form porphyrin and a complex i. e. Mo Cr Nb or W.

[0012] X is a basis used as a ligand of M and Next a methoxy group an ethoxy basis a propoxy group There are an acyloxy group like an alkoxy group like a butoxy group a phenoxy group an aryloxy group like p ******MECHIRU phenoxy group an acetyloxy group a propionyloxy group and a glycyloxy group a fluorine atom a chlorine atom a halogen atom like a bromine atom etc.

[0013] A metal complex of a porphyrin compound expressed with said general formula (II) To a porphyrin compound like 510 1520 ******TETORA phenylporphyrin or 510 and 15 and 20 ******TETORA substituted phenyl porphyrin metal carbonyl For

example molybdenum hexacarbonyl chromium pentacarbonyl niobium pentacarbonyl After making tungsten pentacarbonyl etc. react it can manufacture easily by making alcohol phenol and carboxylic acid contact contacting the output to hydrogen halide according to a request further and crystallizing. A reaction of this porphyrin compound and metal carbonyl can be performed using a solvent for example dimethylformamide according to a request. This reaction is advantageous at a point that go on in a short time of 30 minutes thru/or 2 hours in a room temperature a porphyrin metal complex is obtained with high yield of not less than 65% and moreover refining is also easy.

[0014] In order to make the porosity semiconductor membrane 3 support at least one sort of coloring matter 4 chosen from a porphyrin compound which is general formula (I) or (II) and is expressed and its metal complex After neglecting it until it dissolves this coloring matter in a suitable solvent for example dimethylformamide it carries out the dipping of the porosity semiconductor membrane into this solution and coloring matter fully adsorbs into fine pores of porosity semiconductor membrane this is taken out and it dries after washing if needed.

[0015] Next in this invention solar cell although platinum is preferred as a material of the metal membrane 6 used as a counter electrode a thing

publicly known as a counter electrode of the conventional solar cell such as the other aluminum silver tin and indium can also be used arbitrarily. As for these metal membranes 6 it is preferred to form a physical vapor deposition or by carrying out chemical vacuum deposition on a glass substrate or indium oxide and a tin-oxide complex board.

[0016] In this invention solar cell as an electrolyte inserted between two electrodes although conventionally used as an electrolyte of a solar cell it can choose from inside suitably and can use. An electrolyte used as such a thing with a solar cell using ruthenium bipyridine carboxylic acid coloring matter of gray TSUERO and others mentioned above for example that is there are some which dissolved iodine and potassium iodide in a medium which consists of a mixture of polypropylene carbonate 25 mass % and ethylene carbonate 75 mass %.

[0017] Thickness of the transparent conducting film 2 in this invention solar cell 0.4-0.6 micrometer as for the particle size thickness of 0.01-0.03 micrometer and the metal membrane 6 is chosen in 10-15 micrometers in and 5-30 micrometers of thickness [0.01-0.06 micrometer of / 2-20 micrometers of] of 0.5 micrometer and the porosity semiconductor membrane 3 are preferably chosen in 10-12 micrometers. A range of 8-20 micrometers of thickness of an electrolyte inserted between two electrodes is 10-12 micrometers preferably.

[0018] If a solar cell of such a structure connects between two electrodes with a lead and makes a current circuit form and it irradiates with 420-nm white light from the transparent conducting film side it can be generated with high photoelectric conversion efficiency of not less than 2.9%. Since this photoelectric conversion efficiency is influenced by thickness of each film a state of semiconductor membrane the amount of adsorption of coloring matter electrolytic kind etc. it can be further raised by choosing these optimal conditions.

[0019]

[Example] Next an example explains this invention still in detail.

[0020] The mixture of the reference examples 1510 and 150.5 g (0.6 mmol) of 20 **TETORA (4 **KARUBOKISHI phenyl) porphyrin 0.8 g (3.2 mmol) of molybdenum hexacarbonyl and 100 ml of dry dimethylformamide was refluxed under a nitrogen atmosphere for 2 hours. The stages of progress of the reaction were pursued with the ultraviolet visible spectrum in the meantime. Subsequently the solvent was distilled off after suspending heating and cooling a reaction mixture radiationally to a room temperature. Subsequently the glossy crystal was obtained with the yield of 67% by recrystallizing the solid of dark green obtained by carrying out ionic exchange column chromatography processing and refining a

residue in ethyl alcohol. An ultraviolet visible spectrum and infrared absorption spectrum, ESR ultimate analysis and when mass-spectrum analysis was conducted it was checked that it is a porphyrin metal complex (D) in which X in said general formula (II) corresponds to an ethoxy basis about this crystal M corresponds to Mo and R corresponds to the structure of a hydrogen atom. It processes similarly using 5101520 **TETORA phenylporphyrin or 510 and 15 and 20 **TETORA (4 **SURUHO phenyl) porphyrin as a raw material. The porphyrin metal complex (E) and (F) in which X in said general formula (II) corresponds to an ethoxy basis M corresponds to Mo and R corresponds to the structure of a carboxyl group or a sulfonic group was obtained.

[0021] Into 60 ml of hexane which saturated reference example 2 hydrogen chloride the solution which melted 50 ml of porphyrin metal complexes (E) obtained by the reference example 1 in 15 ml of ethyl alcohol was dropped at the room temperature. The generated crystal was ****(ed) with the glass filter and white crystals were obtained with the yield of 82% by drying after washing by hexane. It was checked that it is a porphyrin metal complex in which X [in / for this thing / said general formula (II)] corresponds to a chlorine atom. An ultraviolet visible spectrum and infrared absorption spectrum, ESR ultimate analysis and when mass-spectrum analysis is conducted M corresponds to Mo and R corresponds to the structure of a carboxyl group.

[0022] Instead of the molybdenum hexacarbonyl in the reference example 3 reference example 1 chromium hexacarbonyl. When it was made to react similarly using niobium hexacarbonyl or tungsten hexacarbonyl the porphyrin metal complex in which Cr Nb or W corresponds [M in general formula (II)] respectively was obtained.

[0023] After dissolving 62.5 ml of example 1 titanium tetraisopropoxide into 10 ml of 2-propanol and the mixture of 380 ml of deionized water and 3 ml of concentration 70 mass % nitric acid and making it hydrolyze in 80 ** for 8 hours evaporation concentration was carried out and the stable titanium oxide colloidal solution was prepared. The particle diameter of this titanium oxide was about 8 nm. As a result of carrying out an X diffraction it turned out that this titanium oxide is an anatase type. On the surface of the sheet metal (25x25 mm) of a 0.5-micrometer-thick indium oxide tin-oxide complex (henceforth [ITO]). The 10-micrometer-thick porous-titanium-oxide film was made to form by carrying out spin coating of the aforementioned colloidal solution 10 g and 2 g of TiO₂ impalpable powder (the product made by Japanese Aerosil trade name "P-25") and a mixture with 2 g of polyethylene glycols and calcinating them at 500 ** for 1 hour.

[0024]5101520 **TETORA phenylporphyrin (A)510 and 1520 **TETORA (4 **KARUBOKISHI phenyl) porphyrin (B)5101520 **TETORA (4 **SURUHO phenyl) porphyrin (C)5101520 **TETORA phenylporphyrin metal complex (D) which were obtained by the reference example 15101520 **TETORA (4 **KARUBOKISHI phenyl) porphyrin metal complex (E) and 510 and 15and 20 **TETORA (4 **SURUHO phenyl) porphyrin metal complex (F) are dissolved in dimethylformamide with 5×10^{-4} molar concentration. After carrying out the dipping of the above-mentioned porous-titanium-oxide film into the prepared solution and neglecting it in 80 ** overnightit took out in argon atmosphereand washed and dried with methyl alcohol.

[0025]As a counter electrodeusing what provided platinum membrane (10 micrometers in thickness) by sputtering process on the ITO board (22x25 mm) as an electrolyteThe solar cell of the structure which shows the iodine 0.38g and the mixture of 2.49 g of potassium iodide in drawing 1 using what was dissolved in the mixture 30g of propylene carbonate 25 mass % and ethylene carbonate 75 mass % was manufactured. Before longthe performance of the solar cell of B and C was as follows.

[0026]

[Table 1]

[0027]

[Effect of the Invention]The dye-sensitized solar cell which can supply the photoelectric current which has high photoelectric conversion efficiency and was moreover stabilized by this invention is provided.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]The sectional view showing one example of the structure of the solar cell of this invention.

[Description of Notations]

- 1 and 7 Transparent substrate
- 2 Transparent conducting film
- 3 Porosity semiconductor membrane
- 4 Coloring matter
- 5 Electrolyte
- 6 Metal membrane
- 8 Current circuit

9 Ammeter
